

# ON THE NECESSARY CONDITIONS FOR THE VALIDITY OF THE HOHENBERG-KOHN THEOREM

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It is shown that the Hohenberg-Kohn lemma and theorem are direct consequences of the statement that the ground state energy (or free energy) of a system of interacting particles in an external field is a unique functional of the potential of this field. This means that, if the Hohenberg-Kohn theorem is valid, the nonuniform density in the equilibrium system and the external field potential are biunique functionals. In this case, the nonuniform density is intimately related to the inverse response function. On this basis, a regular procedure can be constructed for determining the density functional for the free energy or ground state energy.

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In 1964, Hohenberg and Kohn [1] have proved a theorem according to which the ground state energy of inhomogeneous electron gas in a static external field is a unique functional of the nonuniform electron density. The Hohenberg-Kohn theorem is the basis of the density functional theory widely used in various fields of physics and chemistry [2-8]. The Hohenberg-Kohn theorem proof is based on the following lemma [1,9]: the nonuniform density  $n(\mathbf{r})$  in the ground state of a bounded system of interacting electrons in a certain static external field characterized by the potential  $\varphi^{ext}(\mathbf{r})$  uniquely defines this potential. In this case [1,9]:

(a) The term "uniquely" means "with an accuracy up to an additive constant of no interest";

(b) In the case of a degenerate ground state, the lemma relates to the density  $n(\mathbf{r})$  of any ground state. The requirement for the ground state non-degeneracy is easily eliminated [10];

(c) The lemma is mathematically rigorous.

Let us pay attention to statement (c). The lemma proof is based on the strict inequality [1,9]

$$E_1 < E_2 + \int [\varphi_1^{ext}(\mathbf{r}) - \varphi_2^{ext}(\mathbf{r})] n(\mathbf{r}) d\mathbf{r}, \quad (1)$$

Here  $n(\mathbf{r})$  is the density of the non-degenerate ground state of the system of electrons in the potential  $\varphi_1^{ext}(\mathbf{r})$  corresponding to a state with wave function  $\Psi_1$  and energy  $E_1$ ,

$$E_1 = \langle \Psi_1 | H_1 | \Psi_1 \rangle = \int \varphi_1^{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \langle \Psi_1 | T + U | \Psi_1 \rangle, \quad (2)$$

where  $H_1$  is the total Hamiltonian of the system in the external field  $\varphi_1^{ext}(\mathbf{r})$ ,  $T$  and  $U$  are the operators of the kinetic energy and the energy of the interparticle interaction of electrons, respectively. In this case,  $\varphi_2^{ext}(\mathbf{r}) \neq \varphi_1^{ext}(\mathbf{r}) + const$  is the potential of another external field to which the ground state with wave function  $\Psi_2$  and energy  $E_2$  corresponds, which leads to the same density  $n(\mathbf{r})$ . The use of the inequality similar to the strict inequality (1), but with permuted indices, followed by summation of these inequalities, results in a contradiction. This contradiction provides the lemma proof to the contrary [1,9]. However, the strict inequality is a direct consequence of the Rayleigh-Ritz minimum principle which, as applied to quantum mechanics, is written as (see, e.g., [11,12])

$$E_0 \leq \langle \Psi | H | \Psi \rangle, \quad \langle \Psi | \Psi \rangle = 1, \quad (3)$$

where  $E_0$  is the ground state energy of the system of  $N$  interacting electrons with Hamiltonian  $H$  in an external field with potential  $\varphi^{ext}(\mathbf{r})$ , and  $\Psi$  is an arbitrary normalized wave function for the system of  $N$  electrons. In this case, inequality (3) is not strict, which does not allow lemma proof. The problem is what are the conditions of the transition from the non-strict inequality (3) to the strict inequality (1) which is the basis for proving the Hohenberg-Kohn theorem. The first obvious condition is associated with the requirement of the ground state non-degeneracy (see condition (b)). However, satisfying this condition

is insufficient. It should be required that the ground state energy  $E_0$  would be a unique functional of the external field potential  $\varphi^{ext}(\mathbf{r})$ ,

$$E_0 = E_0(\{\varphi^{ext}(\mathbf{r})\}), \quad (4)$$

i.e., as the external field potential  $\varphi^{ext}(\mathbf{r})$  changes, the ground state energy  $E_0$  should take another value. Currently, it seems impossible to prove this statement.

Probably, this problem is intimately related to the problem of  $\varphi$  - representability of the nonuniform density (see, e.g., [13,14]), which was also discussed by W. Kohn in its Nobel lecture [9] **and which has been solved in [15]. It should be mentioned that if the inhomogeneous density  $n(\mathbf{r})$  doesn't  $\varphi^{ext}(\mathbf{r})$ -representative the Hohenberg-Kohn functional cannot be used (see [15] and the literature to this paper). The problem considered in the present paper can be named, by analogy with [15], the  $\varphi^{ext}(\mathbf{r})$ -representability and  $n(\mathbf{r})$ -representability of the ground state energy. It is necessary to stress that the problem of  $\varphi^{ext}(\mathbf{r})$ -representability and  $n(\mathbf{r})$ -representability of the ground state energy is primary for proof of the Hohenberg-Kohn theorem.**

Thus, we come to the conclusion that the Hohenberg-Kohn lemma and theorem are direct consequences of the statement that the ground state energy of a system of interacting particles in an external field is a unique functional of the potential of this field,

$$E_0 = E_0(N\{\varphi^{ext}(\mathbf{r})\}) \rightarrow E_0 = E_0(\{n(\mathbf{r})\}), \quad N = \int n(\mathbf{r})d\mathbf{r}. \quad (5)$$

The impossibility of proving the statement (4) does not cast doubt on the validity of the Hohenberg-Kohn lemma and theorem, but makes it possible to obtain additional consequences under the assumption of their validity. In particular, it follows from (4), (5), and the Hohenberg-Kohn lemma and theorem, that the nonuniform density  $n(\mathbf{r})$  corresponding to the ground state and the external field potential  $\varphi^{ext}(\mathbf{r})$  are biunique functionals,

$$\varphi^{ext}(\mathbf{r}) = \varphi^{ext}(\{n(\mathbf{r})\}) \leftrightarrow n(\mathbf{r}) = n(\{\varphi^{ext}(\mathbf{r})\}). \quad (6)$$

We note that the Hohenberg-Kohn lemma and theorem can be proved within quantum statistics for both the grand canonical ensemble by analyzing corresponding inequalities for the thermodynamic potential [16] and for the canonical ensemble by analyzing corresponding inequalities for the free energy [17]. Thus, we can repeat the above analysis, e.g., for the

free energy  $F$  of a system of  $N$  interacting electrons with Hamiltonian  $H = H_0 + H_1$  at temperature  $T$ . In this case, the inequality (3) takes the following form [18,19] (see also [20]):

$$F \leq F_0 + \langle H_1 \rangle_0, \quad F = T \ln Sp \left[ \exp \left( -\frac{H}{T} \right) \right], \quad (7)$$

$$F_0 = -T \ln Sp \left[ \exp \left( -\frac{H_0}{T} \right) \right], \quad \langle H_1 \rangle_0 \equiv Sp \left[ H_1 \exp \left( -\frac{F_0 - H_0}{T} \right) \right]. \quad (8)$$

In relation (8), the Hamiltonian  $H_1$  smallness is not assumed in any sense. Thus, to prove the Hohenberg-Kohn lemma and theorem for quantum statistics, we come to the necessity of the requirement that the free energy  $F$  of the system of  $N$  interacting electrons at a given temperature  $T$  was a unique functional of the external field potential  $\varphi^{ext}(\mathbf{r})$  (see (4)),

$$F = F(N, T, \{\varphi^{ext}(\mathbf{r})\}). \quad (9)$$

In the limit  $T \rightarrow 0$ , relation (9) obviously transforms into relation (4). A statement similar to (9) can also be formulated for the thermodynamic potential within the grand canonical ensemble. Hence, when condition (9) is satisfied, statement (6) that the nonuniform density  $n(\mathbf{r})$  and the external field potential  $\varphi^{ext}(\mathbf{r})$  are biunique functionals can be generalized for equilibrium systems at a given temperature  $T$  within quantum statistics. Statement (6) makes it possible to obtain relations important for the density functional, whose importance is caused by the absence of the regular procedure of the functional  $F = F(T, \{n(\mathbf{r})\})$  construction, in contrast to the case of the functional  $F = F(N, T, \{\varphi^{ext}(\mathbf{r})\})$  which can be constructed using the perturbation theory diagram technique (see, e.g., [21]), proceeding from the equivalence of the grand canonical and canonical ensembles [22]. In particular, it immediately follows from (6) that (see, e.g., [22])

$$\int \frac{\delta n(\mathbf{r}_1)}{\delta \varphi_{ext}(\mathbf{r})} \frac{\delta \varphi_{ext}(\mathbf{r})}{\delta n(\mathbf{r}_2)} d\mathbf{r} = \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (10)$$

In turn, from the definitions of the free energy  $F$  and nonuniform density  $n(\mathbf{r})$  (see (7), (8)), we find (see, e.g., [21,22]) **the exact relations which are valid for the arbitrary strong external potential  $\varphi_{ext}(\mathbf{r})$**

$$\frac{\delta F}{\delta \varphi_{ext}(\mathbf{r})} = n(\mathbf{r}), \quad \frac{\delta n(\mathbf{r}_1)}{\delta \varphi_{ext}(\mathbf{r}_2)} = \chi(\mathbf{r}_1, \mathbf{r}_2), \quad (11)$$

where  $\chi(\mathbf{r}_1, \mathbf{r}_2)$  is the so-called response function,

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = \int_0^{1/T} \langle \Delta N(\mathbf{r}_1, \tau) \Delta N(\mathbf{r}_2, 0) \rangle d\tau, \quad A(\tau) = \exp(H\tau) A \exp(-H\tau). \quad (12)$$

Here  $\Delta N(\mathbf{r}) = N(\mathbf{r}) - n(\mathbf{r})$ , where  $N(\mathbf{r})$  is the operator of the density of the number of particles. The response function  $\chi(\mathbf{r}_1, \mathbf{r}_2)$  in the Coulomb system is directly related to the static permittivity (see, e.g., [23]); in the classical system, it is related to the pair distribution function (see, e.g., [22]). Furthermore, the response function can be calculated using the quantum field theory methods [21,23]. From (10) and (11), it immediately follows that

$$\frac{\delta \varphi_{ext}(\mathbf{r}_1)}{\delta n(\mathbf{r}_2)} = \chi^{-1}(\mathbf{r}_1, \mathbf{r}_2) \quad \int \chi(\mathbf{r}_1, \mathbf{r}) \chi^{-1}(\mathbf{r}, \mathbf{r}_2) d\mathbf{r} = \delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (13)$$

The second equation in (13) is used to calculate the inverse response function  $\chi^{-1}(\mathbf{r}_1, \mathbf{r}_2)$  which is directly related to the direct correlation function in the classical system (see, e.g., [22]). Under the assumption that the functional for the ground state energy  $E_0(\{n(\mathbf{r})\})$  (or for the free energy  $F(T, \{n(\mathbf{r})\})$ ) is known, the definition of the nonuniform density  $n(\mathbf{r})$  in the density functional theory [1-9] is based on the minimum principle

$$\delta E_0(\{n(\mathbf{r})\}) = 0 \quad (\text{or } \delta F(T, \{n(\mathbf{r})\}) = 0) \quad N = \int n(\mathbf{r}) d\mathbf{r}. \quad (14)$$

The minimality condition (14) at a given number of particles  $N$ , using the Legendre transform, can be written as

$$\frac{\delta E_0(\{n(\mathbf{r})\})}{\delta n(\mathbf{r})} = \text{const} \quad \left( \text{or } \frac{\delta F(T, \{n(\mathbf{r})\})}{\delta n(\mathbf{r})} = \text{const} \right). \quad (15)$$

Taking into account the statement (6), it immediately follows from (15) that

$$\frac{\delta F(\{n(\mathbf{r})\})}{\delta n(\mathbf{r})} = \int \frac{\delta F(T, \{n(\mathbf{r})\})}{\delta \varphi_{ext}(\mathbf{r}_1)} \frac{\delta \varphi_{ext}(\mathbf{r}_1)}{\delta n(\mathbf{r})} d\mathbf{r}_1 = \text{const}. \quad (16)$$

Using now (10) - (13), we find the condition which should be satisfied by the nonuniform density  $n(\mathbf{r})$  of the equilibrium system in the static external field,

$$\int n(\mathbf{r}_1) \chi^{-1}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1 = \text{const}. \quad (17)$$

According to the above consideration, condition (17) can be considered as a necessary condition of the Hohenberg-Kohn lemma and theorem to be valid. In this case, the nonuniform density  $n(\mathbf{r})$  is intimately related to the inverse response function  $\chi^{-1}(\mathbf{r}_1, \mathbf{r}_2)$ , so that

the integral in (17) is independent of the coordinate  $\mathbf{r}$ . Thus, the statement (6) about the biunique correspondence between the nonuniform density  $n(\mathbf{r})$  and the external field potential  $\varphi^{ext}(\mathbf{r})$  in the equilibrium system is a necessary condition for the validity of the Hohenberg-Kohn lemma and theorem, whose direct consequence is the relation (17). Furthermore, the statement (6) in principle makes it possible to solve one of the main problems of the density functional theory, associated with the absence of a regular procedure for determining the functional  $F = F(T, \{n(\mathbf{r})\})$  itself for the free energy, or  $E_0 = E_0(\{n(\mathbf{r})\})$  for the ground state energy. Such a procedure is based on the primary definition of an explicit form of the functionals  $F = F(N, T\{\varphi^{ext}(\mathbf{r})\})$  (or  $E_0 = E_0(N, \{\varphi^{ext}(\mathbf{r})\})$ ) and  $n(\{\varphi(\mathbf{r})\})$ , based on the quantum field theory methods or other regular calculation methods. On this basis, the functional  $\varphi^{ext}(\mathbf{r}) = \varphi^{ext}(\{n(\mathbf{r})\})$  is determined, which is substituted into the found expressions for the free energy  $F = F(N, T\{\varphi^{ext}(\mathbf{r})\})$  (or for the ground state energy  $E_0 = E_0(N, \{\varphi^{ext}(\mathbf{r})\})$ ). This procedure is completely identical to the well-known procedure for constructing the virial equation of state, based on the Mayer diagram technique (see, e.g., [24]).

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